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Comparison of metal additives and Boron atom on MgH_2 absorbing-desorbing characteristics using calculated NQCCs

ABSTRACT

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Using ab initio calculations, the hydrogen desorption from Magnesium hydride (MgH_2) was studied. We presented the calculated nuclear quadrupole coupling constants (NQCCs) of hydrogen atom in various systems of MgH_2 . The effect of interactions of some metal atoms as well as Boron atom with MgH_2 host matrix; (MgH_2+M) nanostructures ($M=Al, Ti, V, Fe, Ni$ and B); were studied and 2H -NQCCs were calculated. From results, introduction of B decreased 2H -NQCC and consequently trend of decrease of charge density in the presence of B was observed. In the other hands introduction of B destabilized initial structure of MgH_2 . But in (MgH_2+M) nanostructures ($M=Al, Ti, V, Fe$ and Ni) the 2H -NQCCs were larger than those of pure MgH_2 and consequently more difficult condition for hydrogen desorption were created. However at sufficiently low B concentration ($Mg_{15}BH_{32}$); the calculation predicted existence of stable dopant system with greater 2H -NQCC. The electric field gradient (EFG) at the site of quadrupolar nuclei were calculated to obtain NQCC parameters at HF/3-21G level of theory.

Keywords: Nuclear quadrupole resonance (NQR); Magnesium hydride (MgH_2); Hydrogen desorption; Ab initio calculations; 2H -NQCC.

INTRODUCTION

Hydrogen is considered to be one of leading candidates for clean energy sources in the future. For safe and efficient hydrogen storage, developments of new hydrogen storage materials are currently being researched [1]. The hydrogen storage capacity per unit weight of typical metal alloys is very low (about 2.0 mass%) and not sufficient for use in a fuel cell vehicle. Among the metal hydrides, Magnesium hydride is one of the most promising candidates as a hydrogen storage media in the automotive industry due to its very high capacity (7.6 wt%) and low cost[1, 2]. Unfortunately, magnesium hydrides are thermodynamically stable, and the dehydrogenation of magnesium hydrides requires high temperatures ($>277^\circ C$).

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Therefore, the practical application is primarily limited by the slow kinetics and the high operating temperature. The possible reasons are that the hydrogen molecules do not readily dissociate on Mg surface and the high thermodynamic stability of Magnesium hydride [3, 4]. Experimentally, great efforts have been made to improve the H₂ absorption and desorption kinetics by mechanically milling MgH₂ and adding transition metals. High-energy ball milling is a suitable technique to affect both the particle size as well as the evolution of a particular crystallite size. Furthermore, different additives, such as liquid milling agents and hard particles, may also have a positive influence on the particle sizes during the milling process. An important group of additives enhancing significantly the absorption and desorption kinetics of nanocrystalline magnesium hydride is the group of a transition metal. Both the catalyst and the nanocrystalline structure with correspondingly high surface area are thought to play important roles in the improvement of hydrogen storage properties. [5–10]. These have been shown to work quite well to obtain the fast hydrogenation of Magnesium as reported by several groups [11–14]. However, in most case, it still requires at least 250 °C to liberate hydrogen from magnesium hydride [15], so the most of research efforts was put toward the ways of efficient and cost effective destabilization of MgH₂ matrix through various dopants introduction, mechanical or even ion beam modification [16-23]. In spite of the many experimental studies of dehydrogenation on MgH₂ surface, little is known about the surface properties and H₂ desorption in MgH₂ system. In order to improve the hydrogen desorption performance, it is clearly useful to understand the fundamental Mg–H bonding properties and the activation barrier for desorption starting from realistic Magnesium.

Nuclear Quadrupolar Resonance (NQR) spectroscopy [24] is a very sensitive technique for determination of electronic charge distribution around quadrupolar nuclei ($I \geq 1$). This method can be used as a probe to obtain information about the environment of a given quadrupolar nuclei and consequently to determine the electronic structure of molecules and complexes.

Quantum mechanical approach has been shown to be a very effective method in determination of the charge distributions in molecules [25, 26].

It seems understanding the bonding nature of magnesium and hydrogen is essential in order to improve its fundamental dehydrogenation performance. Therefore in this work, attention has been focused on the details of the charge distribution on hydrogen atoms of MgH₂ in the presence of some heteroatoms in MgH₂ network; (MgH₂+M) nanostructures (M=Al, Ti, V, Fe, Ni and B). For this purpose, we performed a theoretical investigation on the calculated NQCC parameters of these hydrogen atoms. It is evident that since the bond properties depend on electrons, it is possible to replace hydrogen atoms by deuterium, assuming no structural changes will occur.

These results may give a better understanding of their absorption strength based on their electronic structures.

EXPERIMENTAL

Electric field gradients of Hydrogens were calculated using the Gaussian 03 program [27]. First, the three-dimensional structures of the above mentioned compounds were obtained from the Cambridge Crystallographic Database. Pure MgH₂ compound has crystal structure of rutile [28] (space group number 136, P4₂/mnm, see Figure 1). (MgH₂+M) nanostructures (M=Al, Ti, V, Fe, Ni and B) were obtained by substitution of one of two Mg atoms in original unit cell, thus lowering the symmetry (space group number 65, see Figure 2).

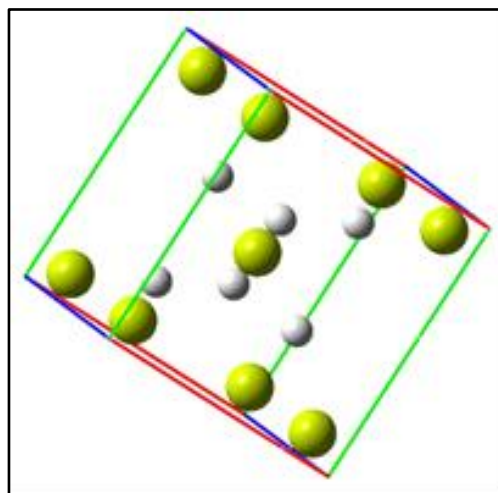


Fig. 1. One unit cell of MgH₂.

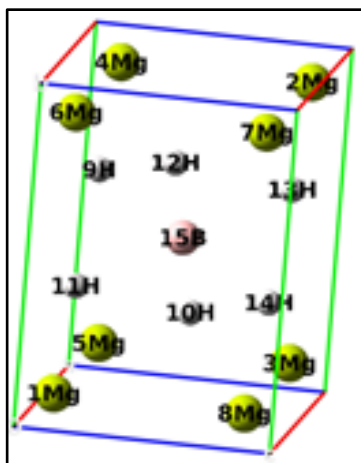


Fig. 2. One unit cell of (MgH₂+M) systems.

After using experimentally established crystal-structure data as input, then an accurate molecular orbital method was applied to the most important part of the studies, i.e., electric field gradient (EFG) calculations. For the sake of CPU time, we apply HF/3-21G level of theory; this level can lead us to a qualitative results. In addition, since there is no experimental data on NQCCs of absorbed hydrogen in MgH₂ unit cells, HF/3-21G is able to lead us to the qualitative results using calculated NQCCs, which seems to be reasonable, because a qualitative prediction may be obtained faster.

Evaluations of NQCCs

The formulation employed in the evaluation of NQR parameters can be found elsewhere [29]. Briefly, the EFG is a traceless, symmetric second-rank tensor that principal axes are chosen so that its components satisfy

$$|q_{zz}| \geq |q_{yy}| \geq |q_{xx}|, \quad (eq_{ij} = \frac{\partial^2 V}{\partial i \partial j}) \quad \text{where } i, j = X, Y, Z,$$

e is electron charge and V is the external electronic potential [24]. The expression $\chi = \frac{e^2 Q q_{zz}}{h}$ is

termed as nuclear quadrupole coupling constant and has the unit of frequency (Hz). h is the Planck's constant, Q is nuclear electric quadrupole moment and q_{zz} is the Z component of EFG tensor in principal axes system. Similar to the many previous studies [25, 26] here we assumed that the nuclear electric quadrupole moments act as a simple constant or scaling parameter, and we do not

parameterize it. Among the wide range of published standard values of quadrupole moments, we selected the recent value of $Q(^2\text{H}) = 2.86 \text{ mb}$ reported by Pyykko [30].

From expression $\chi = \frac{e^2 Q q_{zz}}{h}$, it is obvious that NQCC of nuclei is directly proportional to q_{zz} .

There are two factors controlling the value of q_{zz} in a nucleus; charge density on the nucleus and symmetry of EFG around the quadrupolar nucleus. It is evident that an increase of the charge density causes the q_{zz} and consequently χ , to increase. If charge distribution were such that the symmetry of EFG increased, then q_{zz} and consequently χ will decrease.

RESULTS AND DISCUSSION

MgH₂ is promising compound for hydrogen storage. Its relatively high stability has been the main obstacle for practical applications.

Quadrupolar parameters of nuclei can be used as a useful tool to understand the electronic structure of the compounds. Considering that MgH₂ is classified as ionic material with Mg and H in nearly 2+ and 1- states, respectively, for a strong Mg-H bond, charge transfer from Mg to H must be complete. In the other hands, larger ²H-NQCC dictate: larger charge density on hydrogen and more complete charge transfer from Mg to H and consequently stronger Mg-H bond. Therefore, using calculated NQCCs of hydrogen atoms, the effect of some metal atoms (Al, Ti, V, Fe and Ni) in a unit cell of MgH₂ were compared with that of boron atom.

The results of Table 1 showed that in the presence of boron atom ²H- NQCCs are smaller than those of MgH₂ unit cell (about 20 KHz). This point dictate that the bond strength of Mg-H in MgBH₄ is less than others and therefore desorption of hydrogen in this compound is easier. But in (MgH₂+M) nanostructures (M=Al, Ti, V, Fe and Ni) the ²H- NQCCs were larger than those of pure MgH₂ and consequently more difficult condition for hydrogen desorption are created. Therefore bond strength of Mg-H in MgBH₄ is less than the others and it is expected that desorption of hydrogen in this compound to be easier. But in

(MgH₂+M) nanostructures (M=Al, Ti, V, Fe and Ni), the ²H- NQCCs were larger than those of pure MgH₂ and consequently more difficult condition for desorption were created.

Table 1. The calculated ²H- NQCCs in considered unit cells of MgH₂+M systems.

MgH ₂ +M systems	Calculated ² H- NQCCs (KHz)					
	H9	H10	H11	H12	H13	H14
MgH ₂	49.68	53.98	49.68	53.98	46.21	47.55
MgH ₂ +B	26.96	41.25	28.38	41.25	27.38	25.02
MgH ₂ +Al	51.26	52.75	51.31	52.75	47.74	48.78
MgH ₂ +Ti	61.00	51.62	52.65	51.62	57.52	49.81
MgH ₂ +V	55.18	55.51	50.07	55.51	52.44	48.52
MgH ₂ +Fe	49.94	55.66	50.00	55.66	46.62	48.19
MgH ₂ +Ni	48.10	57.08	47.50	57.08	44.14	46.12

The destabilization of the magnesium hydride by boron atom was due to a weakened bonding between magnesium and hydrogen atoms. Hence the dehydrogenation properties of MgH₂ are expected to be improved to a different extent by the addition of boron atoms.

In continue we have performed ab initio charge density calculations of MgH₂:B dopant systems with various concentrations of boron (Figure 3a). For construction of lower boron concentration structures, supercell approach was used. For Mg₄BH₁₀ compound, supercell of five original unit cells was constructed, in structural arrangement 5×1×1 (space group number 136, P4₂/mnm). The boron atoms are positioned at corners and at center of supercell (Figure 3b). Finally for Mg₁₅BH₃₂ compound, supercell of eight unit cells was constructed, in structural arrangement 2×2×2 (space group number 65, Cmmm). The dopant atoms are positioned at center of two of supercell base planes (Figure 3c). Structural parameters for above mentioned compound are listed in Table 2.

The goal of our work in this part was to investigate the interaction of boron with MgH₂ host matrix, where boron acts as dopant at various concentrations, substituting Mg in its octahedral hydrogen environment. For comparison, ²H-NQCC of pure MgH₂ system has been calculated as well.

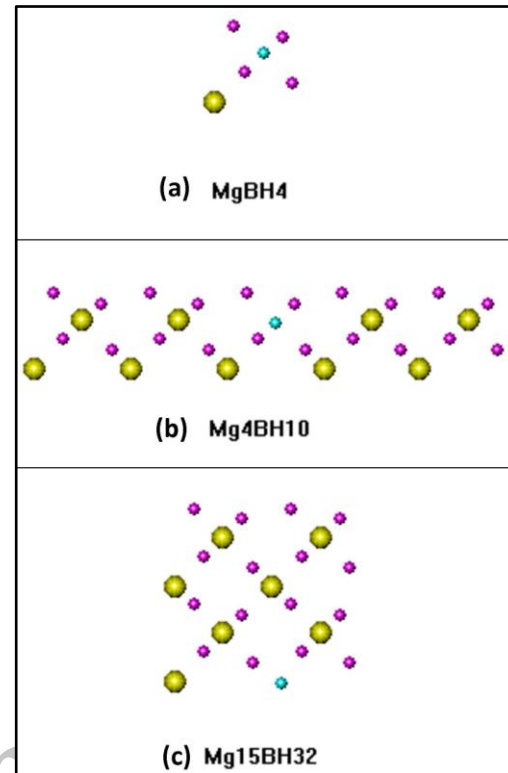


Fig. 3. Unit cells of investigated MgH₂:B dopant systems red balls: Hydrogen, blue balls: Boron, yellow balls: Magnesium; a: MgBH₄ (50 at% B); b: Mg₄BH₁₀ (20 at% B); c: Mg₁₅BH₃₂ (6.25 at% B).

Table 2. Some structural parameters of investigated systems.

structure	Cell parameters		Space group	
	α (A°)	c (A°)	Number	Symbol
MgH ₂	4.518 ^a	3.022 ^a	136	P4 ₂ /mnm
MgBH ₄	4.138	2.767	65	Cmmm
Mg ₄ BH ₁₀	4.465	14.930	136	P4 ₂ /mnm
Mg ₁₅ BH ₃₂	8.930	5.972	65	Cmmm

The results in Table 3 showed that introduction of B decreases ²H-NQCC and consequently trend of decrease of charge density in the presence of B was observed. In the other hands introduction of B destabilized initial structure of MgH₂, however at sufficiently low B concentration (Mg₁₅BH₃₂); the calculation predicted existence of

stable dopant system with greater ^2H -NQCC. It's still considerably high stability can be further decreases by slight increase of B concentration.

Table 3. The calculated ^2H -NQCCs in compound with various concentration of Boron.

Compound	Calculated ^2H -NQCCs (KHz)			
	H1	H2	H3	H4
MgH_2	46.44	34.08	35.37	34.08
MgBH_4	38.17	4.14	2.80	4.14
$\text{Mg}_4\text{BH}_{10}$	36.52	9.30	5.82	35.81
$\text{Mg}_{15}\text{BH}_{32}$	50.10	44.78	48.64	54.27

This result is in agreement with previous findings that introduction of B destabilizes initial structure, and trend of sudden rise of enthalpy of formation with increase of B concentration is observed [31].

CONCLUSIONS

According to the data obtained from charge distributions, it is concluded that:

- Quadrupolar parameters of nuclei can be used as a useful tool to understand the electronic structure of the compounds.

- The results showed that bond strength of Mg-H in MgBH_4 is less than those of pure MgH_2 and it is expected that desorption of hydrogen in this compound to be easier, in the other hands introduction of B destabilizes initial structure of MgH_2 .

- At sufficiently low B concentration ($\text{Mg}_{15}\text{BH}_{32}$); the calculation predicted existence of stable dopant system with greater ^2H -NQCC.

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